

Calculation of semiclassical free energy differences along non-equilibrium classical trajectories

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Abstract

We have derived several relations, which allow the evaluation of the system free energy changes in the leading order in \hbar^2 along classically generated trajectories. The results are formulated in terms of purely classical Hamiltonians and trajectories, so that semiclassical partition functions can be computed, e.g., via classical molecular dynamics simulations. The Hamiltonians, however, contain additional potential-energy terms, which are proportional to \hbar^2 and are temperature-dependent. We discussed the influence of quantum interference on the nonequilibrium work and problems with unambiguous definition of the semiclassical work operator.

I. INTRODUCTION

The nonequilibrium work theorem, or Jarzynski equation, relates nonequilibrium work performed on a dissipative system during certain time interval to the difference of the corresponding equilibrium free energies. Formulated first for classical systems [1, 2, 3], the work theorem has been generalized to the quantum case, too [1, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20]. Monnai and Tasaki have found quantum ($\sim \hbar^2$) corrections to the transient and steady-state fluctuation theorems for a damped harmonic oscillator [21]. Chernyak and Mukamel gave quantum ($\sim \hbar^2$) corrections to the work theorem for a specific form of the driven system Hamiltonian [22]. The quantum generalizations of the work theorem have triggered a certain controversy in the literature on whether it is possible to uniquely define the quantum work operator and how to interpret the quantum work theorem [10, 11, 12, 13, 14, 17, 18].

In the present paper, we use the ideas inspired by the classical work theorems to derive several relations which allow us the calculation of equilibrium semiclassical free energy changes along non-equilibrium classical trajectories. Our aim is twofold. First, we develop a practical tool for the calculation of semiclassical free energies differences through classical equations of motion and/or molecular dynamics simulations. Such semiclassical corrections are responsible, e.g., for the short-distance anomaly of the pair distribution function of liquid neon [23, 24]. Second, we wish to get a better understanding of how quantum interference influences the nonequilibrium work and if it is possible to uniquely define the semiclassical work operator.

Note that all the semiclassical quantities which are considered in the present paper are evaluated in the leading order in \hbar^2 , i.e., with the accuracy $O(\hbar^4)$. We use the symbols h and \hbar intermittently throughout the text, in order to avoid writing numerous factors of 2π .

II. WIGNER DISTRIBUTIONS AND USEFUL IDENTITIES

Let us consider a collection of N quantum point particles with the Hamiltonian

$$\hat{H}(\hat{\mathbf{p}}, \hat{\mathbf{q}}) = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m_i} + U(\hat{\mathbf{q}}). \quad (1)$$

\hat{q}_i , $\hat{p}_i = -i\hbar d/d\hat{q}_i$, and m_i are the positions, momenta, and masses of the particles, $U(\hat{\mathbf{q}})$ is the potential energy. Hereafter, the boldface notation $\hat{\mathbf{p}}$, $\hat{\mathbf{q}}$ is used to collectively denote the set of all \hat{p}_i and \hat{q}_i . We assume that the particles are prepared in an equilibrium canonical ensemble at the temperature T . The corresponding distribution (density matrix) reads

$$\hat{\rho}(\hat{\mathbf{p}}, \hat{\mathbf{q}}) = Z^{-1} \exp\{-\beta \hat{H}(\hat{\mathbf{p}}, \hat{\mathbf{q}})\}, \quad Z = \text{Tr}(\exp\{-\beta \hat{H}(\hat{\mathbf{p}}, \hat{\mathbf{q}})\}), \quad (2)$$

Z being the partition function.

We wish to calculate the leading ($\sim \hbar^2$) corrections to the canonical distribution (2) and partition function Z . To this end, it is convenient to switch to the Wigner representation [25, 26], so that (2) becomes the corresponding Wigner distribution (the subscript W)

$$\rho_W^{(0)}(\mathbf{p}, \mathbf{q}) = Z^{-1} \exp\{-\beta(H(\mathbf{p}, \mathbf{q}) + \hbar^2 \Delta^{(0)}(\beta, \mathbf{p}, \mathbf{q}))\} + O(\hbar^4), \quad (3)$$

$$Z = \int d\mathbf{p} d\mathbf{q} \exp\{-\beta(H(\mathbf{p}, \mathbf{q}) + \hbar^2 \Delta^{(0)}(\beta, \mathbf{p}, \mathbf{q}))\}. \quad (4)$$

Here \mathbf{p} and \mathbf{q} can be treated as the phase variables in the Wigner space, taking the trace reduces to the integration over the Wigner phase space variables, $H(\mathbf{p}, \mathbf{q})$ is the classical Hamiltonian corresponding to its quantum counterpart (1), and $\Delta^{(0)}$ is the temperature-dependent quantum correction [25, 26]

$$\Delta^{(0)} = \sum_{i=1}^N \left\{ \frac{\beta}{8m_i} \frac{\partial^2 U(\mathbf{q})}{\partial q_i^2} - \frac{\beta^2}{24m_i} \left(\frac{\partial U(\mathbf{q})}{\partial q_i} \right)^2 \right\} - \sum_{i,j=1}^N \frac{\beta^2 p_i p_j}{24m_i m_j} \frac{\partial^2 U(\mathbf{q})}{\partial q_i \partial q_j}. \quad (5)$$

For our further purposes we preaverage $\Delta^{(0)}$ over momenta. That is, we replace $p_i p_j$ by $\delta_{ij} m_i / \beta$ and obtain

$$\Delta^{(1)} = \sum_{i=1}^N \left\{ \frac{\beta}{12m_i} \frac{\partial^2 U(\mathbf{q})}{\partial q_i^2} - \frac{\beta^2}{24m_i} \left(\frac{\partial U(\mathbf{q})}{\partial q_i} \right)^2 \right\}. \quad (6)$$

We also introduce two new functions

$$\Delta^{(2)} = \sum_{i=1}^N \left\{ \frac{\beta}{24m_i} \frac{\partial^2 U(\mathbf{q})}{\partial q_i^2} \right\}, \quad (7)$$

$$\Delta^{(3)} = \sum_{i=1}^N \left\{ \frac{\beta^2}{24m_i} \left(\frac{\partial U(\mathbf{q})}{\partial q_i} \right)^2 \right\}. \quad (8)$$

The physical meaning of these new functions will be explained below. Let us now consider the quantities

$$\rho_W^{(a)}(\mathbf{p}, \mathbf{q}) = Z^{-1} \exp\{-\beta(H(\mathbf{p}, \mathbf{q}) + \hbar^2 \Delta^{(a)}(\beta, \mathbf{p}, \mathbf{q}))\}, \quad a = 0, 1, 2, 3. \quad (9)$$

Here $\rho_W^{(0)}$ is the semiclassical Wigner distribution (3) but $\rho_W^{(a)}$ for $a = 1, 2, 3$ are not true semiclassical Wigner distributions [27]. However, all $\rho_W^{(a)}$ share the following evident property: The partition functions

$$Z^{(a)} = \int d\mathbf{p} d\mathbf{q} \exp\{-\beta(H(\mathbf{p}, \mathbf{q}) + h^2 \Delta^{(a)}(\beta, \mathbf{p}, \mathbf{q}))\} \quad (10)$$

coincide with the true semiclassical partition function $Z^{(0)}$ within the accuracy $O(h^4)$. The equivalence of $Z^{(1)}$ and $Z^{(2)}$, $Z^{(3)}$ can be demonstrated via integration by parts,

$$\beta \int d\mathbf{q} \exp\{-\beta U(\mathbf{q})\} \left(\frac{\partial U(\mathbf{q})}{\partial q_i} \right)^2 = \int d\mathbf{q} \exp\{-\beta U(\mathbf{q})\} \frac{\partial^2 U(\mathbf{q})}{\partial q_i^2}.$$

III. SEMICLASSICAL FREE ENERGY CHANGES ALONG CLASSICAL TRAJECTORIES

We are in a position now to derive the semiclassical version of the nonequilibrium work theorem. Let

$$\hat{H}(\hat{\mathbf{p}}, \hat{\mathbf{q}}, t) = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m_i} + U(\hat{\mathbf{q}}, t). \quad (11)$$

be a quantum Hamiltonian, which is allowed to be explicitly time-dependent. Let us now introduce the quantities

$$H^{(a)}(\beta, \mathbf{p}, \mathbf{q}, t) = H(\mathbf{p}, \mathbf{q}, t) + h^2 \Delta^{(a)}(\beta, \mathbf{p}, \mathbf{q}, t), \quad a = 0, 1, 2, 3. \quad (12)$$

Here $H(\mathbf{p}, \mathbf{q}, t)$ is the classical Hamiltonian which corresponds to the quantum Hamiltonian (11), and functions $\Delta^{(a)}(\beta, \mathbf{p}, \mathbf{q}, t)$ are constructed out of $H(\mathbf{p}, \mathbf{q}, t)$ as is prescribed via Eqs. (5)-(8).

Let us now consider $H^{(a)}$ for $a = 1, 2, 3$ as *classical* Hamiltonians which are parametrically temperature-dependent [28]. They can equivalently be rewritten as

$$H^{(a)}(\beta, \mathbf{p}, \mathbf{q}, t) = \sum_{i=1}^N \frac{p_i^2}{2m_i} + U^{(a)}(\beta, \mathbf{q}, t), \quad U^{(a)}(\beta, \mathbf{q}, t) = U(\mathbf{q}, t) + h^2 \Delta^{(a)}(\beta, \mathbf{q}, t). \quad (13)$$

So, the quantum correction gives rise to a simple redefinition of the potential energy, which acquires an additional temperature-dependent $\sim \hbar^2$ contribution. Now we can use the Hamiltonian (13) to write down the corresponding classical equations of motion

$$\frac{dp_i(t)}{dt} = -\frac{H^{(a)}(\beta, \mathbf{p}, \mathbf{q}, t)}{dq_i}, \quad \frac{dq_i(t)}{dt} = \frac{H^{(a)}(\beta, \mathbf{p}, \mathbf{q}, t)}{dp_i} \quad (14)$$

which produce the classical trajectories $\mathbf{p}(t)$, $\mathbf{q}(t)$. Furthermore, we can treat

$$\rho_W^{(a)}(\mathbf{p}, \mathbf{q}, t) = Z_t^{-1} \exp\{-\beta H^{(a)}(\beta, \mathbf{p}, \mathbf{q}, t)\} \quad (15)$$

as the corresponding classical canonical distribution with the partition function

$$Z_t = \int d\mathbf{p} d\mathbf{q} \exp\{-\beta H^{(a)}(\beta, \mathbf{p}, \mathbf{q}, t)\}. \quad (16)$$

After this is done, we can proceed analogously to the derivation of the classical Jarzynski equation [3, 17]. Namely, we can write the following chain of identities:

$$\begin{aligned} \int d\mathbf{p}_0 d\mathbf{q}_0 \exp\{-\beta H^{(a)}(\beta, \mathbf{p}_0, \mathbf{q}_0, 0)\} \exp\{-\beta(H^{(a)}(\beta, \mathbf{p}_t, \mathbf{q}_t, t) - H^{(a)}(\beta, \mathbf{p}_0, \mathbf{q}_0, 0))\} = \\ \int d\mathbf{p}_0 d\mathbf{q}_0 \exp\{-\beta H^{(a)}(\beta, \mathbf{p}_t, \mathbf{q}_t, t)\} = \int d\mathbf{p}_t d\mathbf{q}_t \exp\{-\beta H^{(a)}(\beta, \mathbf{p}_t, \mathbf{q}_t, t)\} = Z_t, \end{aligned} \quad (17)$$

$a = 1, 2, 3$. In deriving Eq. (17) we make use of the fact that motion of a Hamiltonian system can be regarded as the canonical transformation, for which the Liouville theorem holds: $d\mathbf{p}_0 d\mathbf{q}_0 = d\mathbf{p}_t d\mathbf{q}_t$. Introducing the abbreviation

$$\int d\mathbf{p}_0 d\mathbf{q}_0 Z_0^{-1} \exp\{-\beta H^{(a)}(\beta, \mathbf{p}_0, \mathbf{q}_0, 0)\} \dots = \langle \dots \rangle_0 \quad (18)$$

and dividing Eq. (17) by Z_0 , we obtain

$$\langle \exp\{-\beta(H^{(a)}(\beta, \mathbf{p}_t, \mathbf{q}_t, t) - H^{(a)}(\beta, \mathbf{p}_0, \mathbf{q}_0, 0))\} \rangle_0 = Z_t/Z_0, \quad a = 1, 2, 3. \quad (19)$$

We can further split the total Hamiltonian into the system Hamiltonian, the bath Hamiltonian and their coupling,

$$H^{(a)}(\beta, \mathbf{p}, \mathbf{q}, t) = H_S^{(a)}(\beta, \mathbf{p}_S, \mathbf{q}_S, t) + H_B^{(a)}(\beta, \mathbf{p}_B, \mathbf{q}_B) + H_{SB}^{(a)}(\beta, \mathbf{p}_S, \mathbf{q}_S, \mathbf{p}_B, \mathbf{q}_B). \quad (20)$$

Here the system Hamiltonian only is allowed to be explicitly time-dependent. Plugging $H^{(a)}$ (20) into the identity (19) and making use of the equations of motion (14), we can write

$$\begin{aligned} H^{(a)}(\beta, \mathbf{p}_t, \mathbf{q}_t, t) - H^{(a)}(\beta, \mathbf{p}_0, \mathbf{q}_0, 0) = \\ \int_0^t dt' \frac{d}{dt'} H^{(i)}(\beta, \mathbf{p}(t'), \mathbf{q}(t'), t') = \int_0^t dt' \frac{\partial}{\partial t'} H_S^{(i)}(\beta, \mathbf{p}_S(t'), \mathbf{q}_S(t'), t') = W^{(a)}, \end{aligned} \quad (21)$$

$W^{(a)}$ being the work performed on our *classical* system. Thus Eqs. (19) and (21) yield

$$\langle \exp(-\beta W^{(a)}) \rangle_0 = Z_t/Z_0, \quad (22)$$

which is the semiclassical analogue of the classical Jarzynski formula [3].

Note that the ratio of the total ($S + B$) partition functions Z_t/Z_0 equals to the ratio of the system partition functions [3]. Indeed, the reduced system (S) density matrix $\rho_S^{(a)}$ is defined via averaging the total density matrix (15) over the bath degrees of freedom [29, 30]:

$$\rho_S^{(a)}(\mathbf{p}_S, \mathbf{q}_S, t) = Z_{S,t}^{-1} \int d\mathbf{p}_B d\mathbf{q}_B \exp\{-\beta(H^{(a)}(\beta, \mathbf{p}_S, \mathbf{q}_S, \mathbf{p}_B, \mathbf{q}_B) - F_B)\}, \quad (23)$$

where the bath free energy $F_B = -(\ln Z_B)/\beta$ is determined through the bath partition function

$$Z_B = \int d\mathbf{p}_B d\mathbf{q}_B \exp\{-\beta H_B^{(a)}(\beta, \mathbf{p}_B, \mathbf{q}_B)\}. \quad (24)$$

The system partition function in Eq. (23) is explicitly defined as $Z_{S,t} = Z_t/Z_B$ and we can write

$$Z_t/Z_0 = Z_{S,t}/Z_{S,0}. \quad (25)$$

If the quantum $\sim \hbar^2$ corrections are neglected, then Eqs. (19) and (22) reduce, of course, to the classical work theorem for Hamiltonian systems [3].

To illustrate computational aspects of practical use of relations (19,22), we performed "molecular dynamics" simulations for a point particle in one-dimensional nonlinear potential. The quantum Hamiltonian reads

$$H(\hat{p}, \hat{q}, t) = \frac{\hat{p}^2}{2m} + a\hat{q}^2 + b\hat{q}^4 \frac{t}{1+t}. \quad (26)$$

In this example, the mass $m = 1$, the parameters $a = b = 1$, the position \hat{q} , the momentum $\hat{p} = -i\hbar d/d\hat{q}$, the time t , and the Planck constant are taken as dimensionless. We construct the corresponding semiclassical Hamiltonian $H^{(3)}(\beta, p, q, t)$ as is explained in Sections II and III. Then we calculate the free energy difference at times t and 0, $\Delta F = F_t - F_0 = -\ln(Z_t/Z_0)/\beta$, by "molecular dynamics" simulations and "exactly". In "molecular dynamics" simulations, we sample initial values of q and p according to the Wigner distribution (15) (N_{sam} being the number of samplings), solve equations of motions (14) numerically, and calculate the quantity $\exp\{-\beta(H^{(3)}(\beta, p, q, t) - H^{(3)}(\beta, p, q, 0))\}$. The procedure is repeated N_{sam} times, the averaged value $\langle \exp\{-\beta(H^{(3)}(\beta, p, q, t) - H^{(3)}(\beta, p, q, 0))\} \rangle_0$ is obtained, and ΔF is finally calculated through the semiclassical work theorem (19). "Exact" ΔF is obtained through the direct numerical evaluation of the semiclassical partition functions Z_t and Z_0 according to Eq. (16). The results of the calculations are depicted in figure 1. We

see that making $N_{sam} = 10^2$ samplings gives already reasonable, but quite noisy estimation for ΔF (dashed lines), $N_{sam} = 10^3$ gets a better result (dotted lines). $N_{sam} = 10^4$ yields ΔF which is virtually indistinguishable with the exact results (full lines). The convergence is thus rather slow (see Ref. [31] for the comparison of different simulation schemes for obtaining free energy differences). On the other hand, the convergence speed is the same for classical (bottom curves, $h = 0$) and semiclassical (upper curves, $h = 1$) case [32].

The Hamiltonian $H^{(0)}(\beta, \mathbf{p}, \mathbf{q})$, $a = 0$, has already been used in molecular dynamics simulations [33]. Such a choice gives a correct semiclassical distribution, but its practical implementation may encounter certain difficulties [28, 33]. The choice $a = 1$ gives a correct semiclassical distribution over positions \mathbf{q} . The corresponding Hamiltonian $H^{(1)}(\beta, \mathbf{p}, \mathbf{q})$ has also found its application in molecular dynamics simulations, being evaluated up to the terms of the order of \hbar^2 [23] and \hbar^6 [24, 34]. To our knowledge, the Hamiltonians $H^{(2)}(\beta, \mathbf{p}, \mathbf{q})$ and $H^{(3)}(\beta, \mathbf{p}, \mathbf{q})$ have never been used in practice. However, they give more tractable expressions for the semiclassical potential $\Delta^{(a)}(\mathbf{q}, t)$. It should be noted that (almost) all physically relevant potentials $U(\mathbf{q}) \rightarrow 0$ when $|\mathbf{q}| \rightarrow \infty$. In that case, there is no problem with the exponentiating the semiclassical correction potentials, e.g.,

$$\exp\{-\beta H(\mathbf{p}, \mathbf{q}, t)\}(1 + \hbar^2 \beta \Delta^{(a)}(\beta, \mathbf{p}, \mathbf{q}, t)) = \exp\{-\beta H^{(a)}(\beta, \mathbf{p}, \mathbf{q}, t)\} + O(\hbar^4). \quad (27)$$

Such exponentiation may work even beyond its strict domain of validity $O(\hbar^4)$, since it corresponds to the partial summation of the higher order contributions in the semiclassical expansion. If we use strongly attractive potentials, then exponentiation in Eq. (27) for $a = 1$ may not be feasible, since the contribution due to the second term in Eq. (6) may become predominant, so that the exponential explodes. In such a case, the choices $a = 2$ and $a = 3$ are necessary. Finally, a word of caution concerning applications of the present (and similar) semiclassical methods to realistic molecular systems. The ubiquitous presence of sharply varying repulsions in condensed phases means that the terms like (7) and (8) can be quite large. This can lead to numerical difficulties [33]. More fundamentally, this could indicate that a straightforward \hbar^2 -perturbative treatment might not always be appropriate.

IV. DIFFICULTIES WITH THE DEFINITION OF SEMICLASSICAL WORK

Several important points are to be discussed here in connection with the interpretation of our results as semiclassical work theorems. As has been stressed in Sec. II, the distributions $\rho_W^{(a)}(\mathbf{p}, \mathbf{q})$ (9) for $a = 1, 2, 3$ are not true semiclassical Wigner distributions. However, they give correct values of the semiclassical partition functions within the accuracy $O(h^4)$. Furthermore, the Hamiltonian dynamics governed by Eqs. (14) is not, of course, the true semiclassical dynamics. However, if we run classical molecular dynamics simulations with the Hamiltonians $H^{(a)}(\beta, \mathbf{p}, \mathbf{q}, t)$ ($a = 1, 2, 3$) we get correct semiclassical values of the partition functions, again with the accuracy $O(h^4)$.

The explicit form of the semiclassical nonequilibrium "work theorem" (Eqs. (19) and (22)) is not unique. We have simultaneously derived four ($a = 0, 1, 2, 3$) different "work theorems" with different definitions of the work operator $W^{(a)}$ (21). For each particular choice of the classical Hamiltonian, $W^{(a)}$ can definitely be treated as the classical work, and all $W^{(a)}$ coincide in the limit $\hbar \rightarrow 0$. However, we cannot regard any of $W^{(a)}$ as a true semiclassical work operator. First, $W^{(a)}$ for $a = 0, 1, 2, 3$ yield different values of work, and it is not clear which choice (if any) is preferable. Second, the mean value of the work operator $\overline{W}^{(a)}$ does not coincide with the mean semiclassical energy difference ΔE . Indeed, adopting the notation

$$\int d\mathbf{p}_t d\mathbf{q}_t Z_t^{-1} \exp\{-\beta H^{(a)}(\beta, \mathbf{p}_t, \mathbf{q}_t, t)\} \dots = \langle \dots \rangle_t, \quad (28)$$

we can explicitly define

$$\overline{W}^{(a)} = \langle H^{(a)}(\beta, \mathbf{p}_t, \mathbf{q}_t, t) \rangle_t - \langle H^{(a)}(\beta, \mathbf{p}_0, \mathbf{q}_0, 0) \rangle_0 \quad (29)$$

and

$$\Delta E = \langle H(\beta, \mathbf{p}_t, \mathbf{q}_t, t) \rangle_t - \langle H(\beta, \mathbf{p}_0, \mathbf{q}_0, 0) \rangle_0. \quad (30)$$

Therefore,

$$\overline{W}^{(a)} = \Delta E + h^2 \{ \langle \Delta^{(a)}(\beta, \mathbf{q}_t, t) \rangle_t - \langle \Delta^{(a)}(\beta, \mathbf{q}_0, 0) \rangle_0 \}. \quad (31)$$

The difference between $W^{(a)}$ and ΔE is of the order of h^2 and is generally nonzero [35]. This is the semiclassical way of stating that it is hardly possible to properly and unambiguously define the quantum work operator [10, 11, 12, 13, 14, 17, 18].

It is important that $W^{(a)}$ (21) is explicitly temperature dependent. That is a direct consequence of quantum interference. In classical case, we can consider a single trajectory in the phase space and calculate the work along it. Such a work is determined exclusively by the difference of energies along the trajectory. Incoherent summation over many such trajectories, weighted via classical canonical distribution, yields the classical work theorem. In quantum or even semiclassical case, there exists interference between the trajectories, which manifests itself through the temperature dependent Hamiltonians $H^{(a)}(\beta, \mathbf{p}, \mathbf{q}, t)$. Thus, even in the semiclassical limit, it is not possible to define $W^{(a)}$ as a function of exclusively the phase space variables and time. The ensemble quantity, viz., the temperature, inevitably enters the definition of work.

The semiclassical Jarzynski equations (19) and (22) cannot be directly considered as semiclassical versions of the quantum Jarzynski equation [1, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20]. Indeed, the latter is written as [11]

$$\left\langle \exp(\beta \hat{H}(0)) \exp(-\beta \hat{H}(t)) \right\rangle = \mathcal{T}_< \left\langle \exp(-\beta \hat{W}) \right\rangle = Z_t/Z_0. \quad (32)$$

Here $\hat{H}(t)$ is the total Hamiltonian in the Heisenberg representation, $\langle \dots \rangle = \text{Tr}(\exp\{-\beta \hat{H}(0)\} \dots)$, and $\mathcal{T}_>$ is the chronological ordering operator. The trajectory-dependent work operator is explicitly defined as [17, 18]

$$\hat{W} = \hat{H}(t) - \hat{H}(0) = \int_0^t dt' \frac{d}{dt'} \hat{H}(t') = \int_0^t dt' \frac{\partial}{\partial t'} \hat{H}_S(t') \quad (33)$$

(the last expression in Eq. (33) holds true provided we partition the total Hamiltonian as a sum of the system Hamiltonian, bath Hamiltonian and their coupling, and assume that the system Hamiltonian is explicitly time dependent, $H(t) = H_S(t) + H_B + H_{SB}$). In principle, we can write down a direct semiclassical analogue of Eq. (32). The corresponding formulas are not presented here, since they are quite cumbersome and difficult to interpret. What is even more important, we have to introduce the semiclassical time-evolution operator, which should be evaluated in the leading order in \hbar^2 . That would prevent us from a simple classical interpretation of the formulas.

V. CONCLUSIONS

We have derived semiclassical analogues (19) and (22) of the classical work theorems, which allow us to evaluate the ratio of the (system) partition functions in the leading order

in \hbar^2 , with the accuracy $O(\hbar^4)$. The corrections due to the quantum statistics (Bose-Einstein or Fermi-Dirac) give rise to the contributions $\sim \hbar^3$ to the equilibrium density matrices and partition functions [36] and are not considered here.

The semiclassical analogues of the work theorems are formulated in terms of purely classical Hamiltonians $H^{(a)}(\beta, \mathbf{p}, \mathbf{q})$ (12) and classical trajectories, so that semiclassical partition functions can be evaluated, e.g., via classical molecular dynamics simulations. The Hamiltonians, however, contain additional potential-energy terms, which are proportional to \hbar^2 and are temperature-dependent. The Hamiltonians $H^{(0)}(\beta, \mathbf{p}, \mathbf{q})$ and $H^{(1)}(\beta, \mathbf{p}, \mathbf{q})$ have already been used in classical, the so-called Wigner-Kirkwood, molecular dynamics simulations (see Refs. [33, 37] and [23, 24, 34], correspondingly). Conceptually similar are also the Feynman-Hibbs molecular dynamics [38] and the quantized Hamilton dynamics [39]. We mention also that the use of the path integral technique in dynamical computer simulations necessitates introducing additional fictitious classical degrees of freedom into the system under study. For example, the ring polymer molecular dynamics is based on the classical evolution of the polymer beads [37, 40, 41]. The path integrals have recently been applied to the calculation of partition functions through the quantum work theorem [42, 43]. In our semiclassical method, no additional degrees of freedom are introduced. Furthermore, the higher order in \hbar^2 contributions can straightforwardly be incorporated into our main formulas (19) and (22), if necessary. For example, $H^{(1)}(\beta, \mathbf{p}, \mathbf{q})$ evaluated up to the terms of the order of \hbar^6 has been used in Refs. [24, 34].

The explicit form of the semiclassical work theorem (Eqs. (19) and (22)) is not unique. In fact, we have derived four ($a = 0, 1, 2, 3$) different work theorems with different definitions of the work operator $W^{(a)}$ (21). For each particular choice of the classical Hamiltonian $H^{(a)}(\beta, \mathbf{p}, \mathbf{q})$, $W^{(a)}$ can definitely be treated as the classical work, and all $W^{(a)}$ coincide in the limit $\hbar \rightarrow 0$. However, we cannot claim any of $W^{(a)}$ to be a true semiclassical work operator. First, $W^{(a)}$ yield different values of the work performed, and it is not clear which choice (if any) is preferable. Second, the mean value of the work operator $\overline{W}^{(a)}$ (29) does not generally coincide with the mean semiclassical energy difference ΔE (30). This indicates, at the semiclassical level, that it is hardly possible to properly and unambiguously define the quantum work operator [10, 11, 12, 13, 14, 17, 18]. However, the ambiguity in the physical meaning of the quantity $W^{(a)}$ does not prevent us from using the semiclassical work theorem in practical calculations and classical molecular dynamics simulations, in order to get the

system free energy differences or semiclassical averages.

Note finally that the present approach can be incorporated into a general scheme developed in [17] to generate semiclassical versions of different fluctuation theorems for Hamiltonian systems in the equilibrium and in a steady state. For example, treating the Hamiltonians (20) as true classical Hamiltonians, we can straightforwardly derive the semiclassical counterpart of the Crooks transient fluctuation theorem [44, 45]:

$$\langle \delta(w - W^{(a)}(\mathbf{p}_0, \mathbf{q}_0, t)) \rangle_0 = \langle \delta(w + W^{(a)}(\mathbf{p}_t, \mathbf{q}_t, t)) \rangle_t \exp(\beta w) Z_t / Z_0. \quad (34)$$

Here $W^{(a)}(\mathbf{p}_0, \mathbf{q}_0, t)$ and $W^{(a)}(\mathbf{p}_t, \mathbf{q}_t, t)$ is the classical work (21) expressed as the function of the initial and final coordinates, correspondingly.

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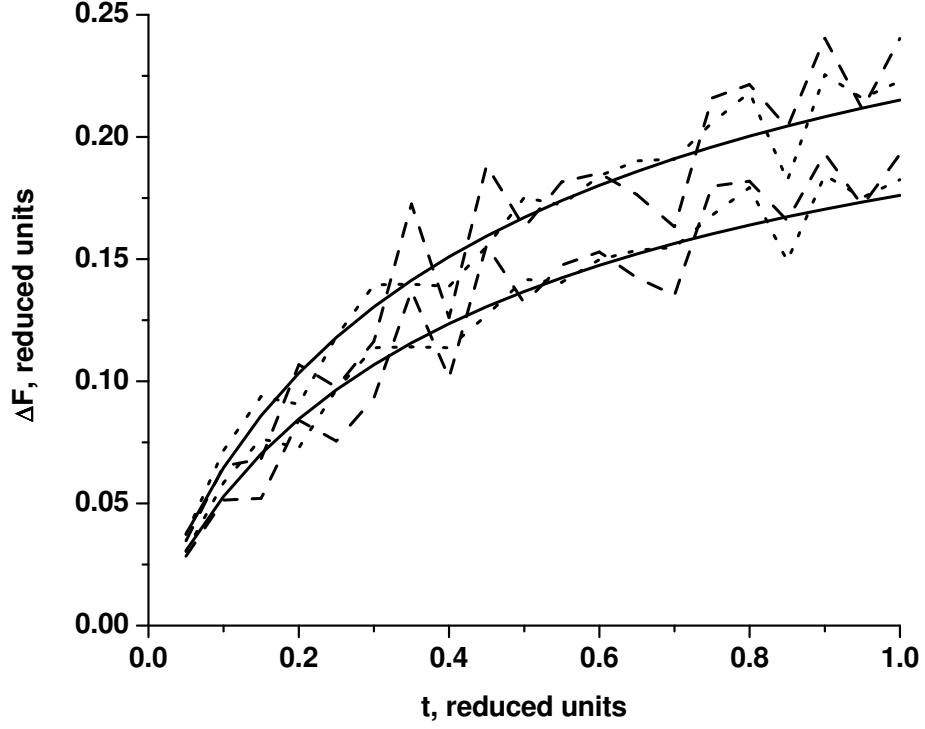


FIG. 1: The difference between the free energies at times t and 0, $\Delta F = F_t - F_0 = -\ln(Z_t/Z_0)/\beta$, as a function of t . The lower curves show the classical result ($\hbar = 0$) and the upper curves show the semiclassical result ($\hbar = 1$). Full lines correspond to "exact" semiclassical calculations, dashed and dotted lines correspond to "molecular dynamics" simulations (see text for details).